



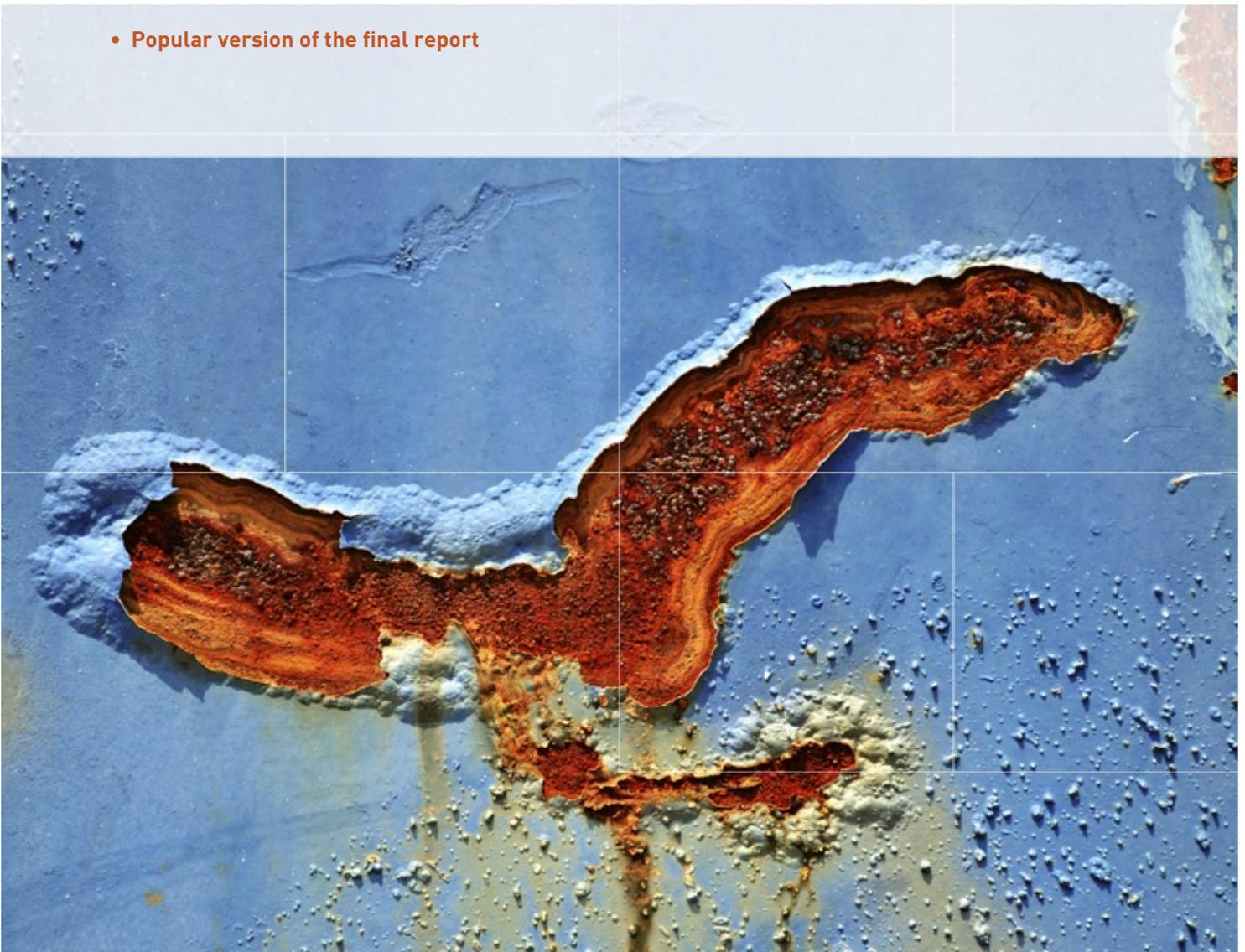
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Nanosized Particles for Improved Scratch Resistance of Polymeric Materials

- Popular version of the final report



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Abstract:		
<p>Scratch and mar resistance of plastic articles is a main attribute in Nordic industry with products in the premium category. Technology for improving the properties with particulate nano additives in polymers will create product benefits for either base materials or coatings. Costs and weight reductions with maintained or improved properties are prime targets but environment aspects are also focused. An effective way for improvements is offered by nanosized particles but knowledge is limited and applied research is needed.</p> <p>The objective of the project consortium was to work together in developing scratch- and mar resistant nano-composites for polymers. Characterisation methods and designing of selection criteria for optimal particle/polymer systems were established for selected systems. Consideration of health & safety and environmental aspects has been included. Dissemination of technical information about the nanosized fillers potential was ensured as appropriate within the Nordic region.</p>		
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Executive summary

The main vision of NANOREP project was to establish a strong network of expertise in the field of highly scratch and mar resistant polymer materials based on nanosized particles in the Nordic countries.

The main technical objectives of the project were:

- To develop a range of polymer blends with nanosized particles for enhanced scratch resistance in the polymer families decided by the consortium.
- To select appropriate methods for the characterization of scratch resistance according to product specifications defined by the consortium members.
- To develop and manufacture nanoparticles identified to be of interest in the consortium. Environmental and health aspects were considered.
- To arrange meetings, diffuse literature and reports to make technology transfer within the nanoparticle area from academic and research environment to the industry.

The study achieved the main vision by:

- Creating clusters inside the consortium
- Arranging technical meetings
- Contacting new R&D expert groups
- Contacting new industries
- Selecting a range of nanosized particles and thermosets in the consortium for clarifying the effect of improving scratch resistance
- Screening out the most promising systems

Method/Implementation:

The project was divided into three main tasks:

- Task 1: Characterization of lacquer and paint systems. Characterization and modification of nanosized materials
- Task 2: Modification of lacquer and paint systems
- Task 3: Testing and evaluation of the scratch/mar resistance

Results and conclusions

The Following success criteria have been reviewed:

1. Develop a range of polymer blends with nanosized particles for enhanced scratch resistance

The target was to improve the scratch resistance by at least a factor of 3 as measured by the Erichsen pen method. The target of improving thermosets was achieved in various grades depending on the types of coatings: from no improvement to significant improvement of the scratch resistance could be reached.

Coatings for consumer electronics applications:

- High demanding specifications and hard reference coatings
- No modification has been done beyond the screening test
- No improvements with nanoparticles yet

Coatings for concrete flooring:

- Little improvement is observed with some nanoparticle systems

Coatings from interior trim/wall/floor applications:

- Significant improvements have been observed when some test methods are used

2. Select appropriate methods for the characterization of scratch and mar resistance

Several characterization methods have been selected according to the application of the coating as described in Chapter 6.

3. Develop and manufacture nanoparticles identified to be of interest in the consortium

The nanoparticles developed and tested during the project are described in chapter 4.1.1.

4. Cover environmental and health aspects

The HSE aspects linked to use of nanoparticles are summarized in Chapter seven.

7. Arrange meetings, diffuse literature and reports to make technology transfer from academic and research to industry

An eRoom was created where all the information distributed among the partners was gathered.

SINTEF presented the NANOREP project to the NANOTECH conference in Helsinki in 2007.

IVF presented the NANOREP project to an internal seminar involving invited industrial partners in September 2007.

SINTEF contributed to an Open hearing arranged by the Technology Council about HSE aspects related to Nanomaterials in 2007.

A Web page for NANOREP project is under preparation.

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1 Problem description

In contrast to metals and ceramics, polymers are relatively inexpensive, light-weight materials which can be processed into various shapes with broad fields of applications – textiles, packaging, automotive parts, furniture and different industrial and household appliances - as well applied as paints and coatings. However, polymers have some important drawbacks compared to metals and ceramics such as limited wear and scratch resistance and low stiffness and strength. Emerging nanotechnologies offer the opportunity to upgrade mechanical properties of polymers at a very low concentration when incorporating specifically designed and/or processed nano-particles.

Companies in the Nordic region are preferably operating in niches of a high quality level with high requirements on surfaces. Scratch and mar resistance of those products are very important properties. Cars and electronic devices are examples where the visual aspect may be highly affected by these properties. Coatings used in the furniture and construction sector are other good examples of this. In addition to the visual aspect, scratch resistance is also related to other performance properties – such as friction and wear. It will also affect the product life cycle as surface appearance limits the lifetime for many products. In product assembly, damage is also causing rejects due to scratch and mar.

A large-scale technological breakthrough came in the late 1980s when Toyota started to use nanocomposite-based parts in some of their volume models. One of the most recent efforts include GM working with several partners with nano-fillers in nanocomposites for applications like claddings and facia – benefiting from mass savings (7-21 %), improved appearance, reduced paint delamination and better recyclability. Next to be commercialized may be many other critical components such as mobile phone cases and other parts within the telecom industry. The focus in this progressing development has been on mechanical properties while scratch and mar resistance has not been prime targets.

Development of nanoparticle-based paints is also progressing to the stage of practical usage, i.e. for heat exchangers and automobile wheel rims. In addition to improved mechanical properties such as scratch resistance, paints can be applied in thinner layer, down to 5- 25 micrometers – that also means substantially lower paint consumption and less organic solvent emission. The development and commercialisation of nanoparticle systems has been carried out parallel. One example is the German company Wacker, which recently introduced a series of silicone based particles in the nanosize range under the brand name of Genioperl. Many applications are targeted, among them coatings and paints for cars to make them resistant to grits flying up from the road. Finally nanoparticles smaller than the wavelength of visible light (< 20nm) appear as “transparent”.

To create premium surfaces of plastic components, painting is used with added costs and environmental impact as drawback. Upgrading the polymers with nanoparticles could make painting unnecessary. Using more exclusive polymers also creates the premium surfaces and this could also be addressed by nanoparticles so that low cost polymers could be used. The nano surface quality tool will extend the property range of polymers and can also be used for making single polymer concepts which will facilitate recycling.

Producers and users of plastic articles will have great use of the nano particle tool. Keeping updated with a fast and continuously expanding nanotechnology platform is a difficult issue. The competitive edge of the entities will depend on their ability to absorb this powerful technology.

The present project called "NANOREP" contributed to build up a consortium of expertise in the fields of improving scratch/mar resistance in polymer materials with nanoparticles, and testing/characterizations of nanostructured materials.

2 Objectives

The main vision of NANOREP project will be to establish a strong network of expertise in the field of highly scratch and mar resistant polymer materials based on nanosized particles in the Nordic countries.

The technical objectives of the project are:

- Develop a range of polymer blends with nano-particles for enhanced scratch resistance in the polymer families decided by the consortium. Both water or solvent-based coatings and thermoplastic systems shall be covered. The polymer-particle compatibility shall be optimized for inter adhesion. The target is to improve the scratch resistance by at least a factor of three as measured with the selected measuring methods.
- Select appropriate methods for the characterization of scratch and mar resistance according to product specifications defined by the consortium members. Damage mechanisms will be studied on the nanosized level. Visual effects caused by various damage origins like scuff, mar and ploughing scratch shall be covered.
- Investigate and develop dispersion methods for the polymer systems with the various types of nanoparticle.
- Develop and manufacture nanoparticles identified to be of interest in the consortium. The step will include identification and characterization of nanoparticles for increase of the scratch resistance and also create understanding of the mechanisms of their function. Environmental and health aspects shall be covered as also the cost situation.
- Arrange meetings, diffuse literature and reports to make technology transfer within the nanoparticle area from academic and research environment to the industry.

3 Organisation and selection of applications

The organisation layout was as follows:

Two main types of polymers were addressed in the overall project: Paints/Lacquers and thermoplastics.

To answer to the advice from the Nordic Innovation Centre to focus the activities on fewer polymeric material application areas (ref. invitation letter to submit a final project proposal dated 01.03.2006), we decided to divide the project into 2 phases: Phase I focusing on paints and lacquers applications (this project) and Phase II focusing on thermoplastics applications.

SINTEF was coordinator of the project.

Phase I included the participation of 6 industrial partners, where 2 were producers of nanoparticles (ELKEM and EKA), 3 were producers of paints and lacquers (JOTUN,

BECKERS and MALNING) and 1 was end users (BANG & OLUFSEN) and 3 research institutes (SINTEF, IVF and ICETEC).

The 3 research institutes contributed mainly to the characterisation of raw materials and the modification of a defined set of paint/lacquers by nanoparticles. In addition SINTEF developed a new and patented technology to produce nanoparticles that improve scratch resistance of polymer materials.

Phase II was extending the consortium presented in phase I with additional R&D institutes and industries from the Nordic countries. Phase II is planned to start in 2008 and end in 2010.

The project was divided into three interdependent tasks:

- Task1: Characterization of lacquer and paint systems. Characterization and modification of nanosized materials
- Task 2: Modification of lacquer and paint systems
- Task 3: Testing and evaluation of the scratch/mar resistance

In task 1, relevant lacquer and paint systems were selected. Selected properties according to specifications of the products were characterized by methods applied in the consortium. Similarly a range of nanosized particle systems was selected within the consortium and characterised. Commercially available nanosized particles were chosen as reference materials.

In task 2, the paints and lacquers selected and characterised in task 1 were modified by nanosized particles. A screening test was performed to select the most promising candidates.

In task 3, the mechanism of scratch formation during testing was studied in more details.

4 Selected nanosized materials and characterisation methods

4.1 Nanosized particles tested in the project

4.1.1 Experimental and commercial materials from the consortium

Water based sols from EKA Chemicals: 2 commercial sols (CC15 and CC30) and 1 experimental sol were used.

Powders and dispersions (water based and solvent based) from Elkem Materials: 8 experimental products in powder and dispersion forms were tested.

Sols from SINTEF: 4 experimental sols (water based and solvent based) were applied.

4.1.2 Commercially available systems from outside the consortium

Nanoparticles from Byk Chemie were tested as a reference material in the project. Other materials from Grace, Rhodigard and Micro Powders were tested as well.

4.1.3 Characterization methods of nanosized particles

The particulate systems described as nanosized particles belong to the size range of typically 1-500 nm. Above this range the particles are usually described as submicron (sub-micrometre) size materials. When the size of a particle is reduced to the nanosized range, the surface-to-volume

ratio is increased to a level at which the positive free surface energy becomes a significant quantity. This leads to a strong particle-particle interaction – agglomeration.

The task of characterization of the nanoparticles is related to their state of delivery – solid or liquid. The solid material usually needs to be dispersed in a liquid. This operation is very critical as it includes breaking down of the strong agglomerates. The dispersibility of the nanosized system may thus turn out to be an important part of the characterization task.

There are also other particle assemblies (in-situ generated nano-dispersions and other concepts, e.g. nanobuilding blocks).

The purpose of the characterization is most often to assess the contribution of nanosized powders compared with larger-sized powders. The main features to determine are the particle morphology, size, and size distribution. Also the surface area and surface chemistry must be evaluated. In the literature it may be concluded that a number of books and articles address the topic but only a few of these deal with the difficulties and limitations encountered.

4.1.3.1 Nanoparticle classification

Nanoparticles are usually classified into the following groups:

- Nanoclays
- Colloidal and other silica's
- Other metal oxide nanoparticles
- Carbon Nanotubes (CNT)
- Other nano-systems (fullerenes, nanocapsules, nanofibers, nanoporous particles)

4.1.3.2 Characterization methods

The list of characterization methods below is mainly limited to the systems of interest for lacquers and paints. Another limitation is that the focus is on the starting particles, it appears more appropriate to deal with the characterization of the dispersed systems under the second paragraph concerned with dispersion and modification.

1/ Particle size distribution

- *Sedimentation* (less applicable to nano-range)
- *Light scattering methods* - e.g., dynamic light scattering [DLS] and static laser scattering [SLS] offer rapid measurement of particle size and size distributions of sub micrometre-sized powders. Such methods measure either the spatial or the temporal variation of scattered light. In SLS, particles suspended in a fluid are exposed to a laser, and both the amount of light scattered and the scattering angle are measured. Once calibrations of the response coefficients of the scattering light and detectors are known, the measured intensity distribution of the scattered light can be converted into a particle size distribution. DLS: used for finer particles with a range of 3 nm-6 micron. Iterative fitting operations of known frequency distribution functions (of particles with various known sizes) are applied to that of the unknown frequency distribution to obtain the particle size distribution.

Sources of error: SLS - difficult to collect light at high scatter angles associated with nanosized particles; limited to a size range of 20 nm-1,000 μm .

2/ Specific Surface Area (BET; single or multi-point)

Usually nitrogen or argon gas adsorption analysis; well-reproducible for the selected representative powder sample; degassing important, for nanosized particles with a high surface energy a high de-gassing T (- 200 C) & vacuum is appropriate.

Multipoint rather than single-point BET surface area analysis in order to collect full adsorption isotherms should be preferred (in order to identify *nano-porosity* in the powders). Calculation of the equivalent area diameter can then be of interest to get an estimate of particle size.

Error source: adsorption of nitrogen or capillary condensation in interparticle voids can result in erroneous measurements.

3/ Porosimetry

As above; this method is used to identify possible particle/agglomerate internal porosity structure. In addition to traditional mercury porosimetry methods (and BET-based methods according to the above item), there are new techniques available such as Environmental ellipsometric porosimetry (EEP). This method consists of allowing the system to stand in an atmosphere where the relative humidity is controlled. The refractive index and the thickness of the particle films are measured in the visible wavelength range during increasing and decreasing relative humidity.

4/ Diffraction methods

Diffraction-based techniques (e.g., x-ray diffraction [XRD] and neutron diffraction [ND]) determine crystallite size. Small Angle Neutron Scattering (SANS) (or SAXS, Small-Angle X-ray Scattering) can theoretically provide information about aggregate size, particle morphology, size distribution, surface area, total pore volume and the thickness of a surface layer. However, the size range is limited from 1 nm to about 300 μm (1 nm-2 μm for SAXS). According to the opinion expressed in the literature, pre-screening for larger particles should be done. If the particles are very uniform in both size and shape, it is difficult to determine the size and shape of the powders from SANS alone.

* X-ray Diffraction (XRD)

peak broadening analysis as a function of mean particle size; The instrumental broadening is determined by using both coarser size powder of the same material with a reference powder material with peaks within the same angle range. After subtracting the instrumental broadening contribution from the nano-powder peaks, Scherrer's equation is used to determine the particle size.

* Neutron-Based Methods

Diffraction techniques where neutrons are scattered by single crystal monochromators. Measurements of particle size, local strain, and lattice strain distributions are obtained from the intensity, I_{ND} , versus (the reciprocal wave vector range, Q) Q_{ND} data.

Error source: if the nanopowder is polycrystalline, the result may be different than the apparent particle size

5/ Electron Microscopy Techniques

Imaging techniques including particle preparation & automated image analysis

- Field Emission Electron Scanning Microscopy (FESEM)
- Transmission electron microscopy (TEM)
- Electron energy loss spectroscopy (EELS)
- Atomic force microscopy (AFM)
- Energy dispersive X-ray spectroscopy (EDS)

Error sources: field emission scanning electron microscopy (FESEM) and other electron or optical microscopy techniques analyze small samples that may not be representative of the bulk powder material.

6/ Atomic Force Microscopy (AFM)

AFM sample preparation techniques are similar to those for optical or SEM/TEM methods but much simpler and less time-consuming. The appropriate surface treatment however is quite important. In addition to compact systems, individual particle size characterization is considered both cost- and time efficient – while the AFM resolution is comparable or better than traditional techniques.

Main advantage: morphology determination, direct measurements of volume and 3D display.

Further advantages of using AFM are said to be:

- faster than SEM or TEM
- providing directly a 3D mapping
- more affordable instrumentation
- works on many nanoparticle types & different nanoparticle systems

Critical features: sample preparation in order to obtain good resolution images, the requirements include: rigid adherence + good dispersion of the particles on the substrate, the substrate roughness less than the size of the nanoparticles.

4.1.3.3 Paint-specific characterization methods

There are many characterization methods for slurries and coatings. In our work we may need to focus on those which can be anticipated to be of relevance to the nano-systems, i.e. where the addition of nano-fillers can be expected to modify the chemical or physical response of these systems.

1/ *Slurries*

- pot lifetime/storage stability
- VOC/Solid content
- (wetting angle?)

2/ *Coatings*

- Contact angle measurement
- Hardness
- Adherence
- Gloss60Deg
- Fineness
- Flexibility
- Drying time
- Colour change (stability)

4.1.4 Example of characterisation of the rheological properties of modified coating systems

The curing of a two component epoxy was characterised by viscoelastic measurements. Fig. 1 shows the variation of the storage modulus as a function of time measured after mixing of an epoxy resin and a hardener for 2 ours at 35°C. The systems that have cured for 3h and 24h before measurement showed a higher elastic modulus.

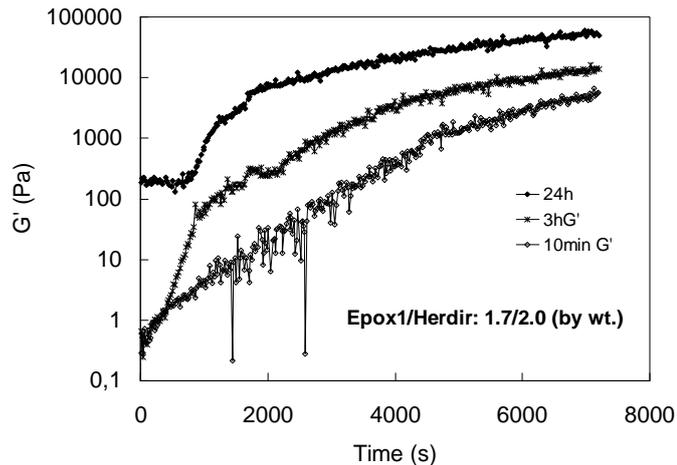


Figure 1. Storage modulus as a function of time after mixing of epoxy resin and hardener for 2 hours at 35°C.

Fig. 2 shows the variation of the storage modulus with time for the same system containing different types of nanosized particles from EKA Chemicals. The addition of nanosized particles results in higher elastic modulus. This indicates a strong interaction during curing and the curing starts earlier. When comparing Fig. 1 and Fig. 2, the addition of 15% CC30 reaches the final level of reference in half of the time.

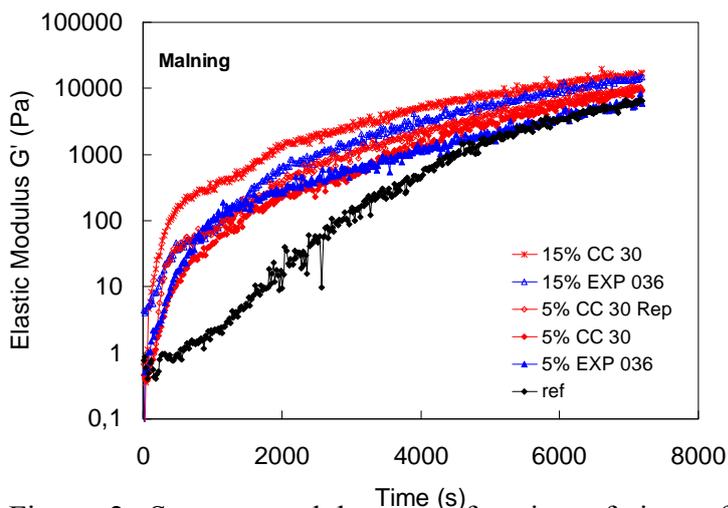


Figure 2. Storage modulus as a function of time after mixing of epoxy resin and hardener modified with nanoparticles for 2 hours at 35°C.

5 Modification of paints and lacquers

Three relevant applications in the consortium were selected: Hardwood flooring, trims and consumer electronics.

The following paints and lacquers were selected:

- Water borne acrylic/PUR lacquer
- Water borne acrylic paint
- Solvent borne PUR clear lacquer
- 2-component PUR paint
- Water borne epoxy 2 component paint, clear and white
- UV cured clear coat solvent borne

- Soft-feel PUR solvent borne
- Acrylic clear coat solvent borne
- Polyurethane water borne

5.1 Modification methods of nanosized materials

The high surface activity is a key aspect of nanomaterials. Agglomeration and aggregation is highly detrimental - blocking the surface area from contact with the coating polymers. Only well dispersed or singly dispersed particles allow utilizing the full beneficial potential of the particles. As most nanomaterials are still fairly expensive, this aspect is of high importance also for the commercialization of product formulations containing nanomaterials.

Since the nano-level is comparable to the size range of many molecular systems such as polymers the interaction energy between the particles is comparable to that of the interaction of macromolecules.

This energy can be minimized by:

- 1/ a particle-to-particle interaction – agglomeration or
- 2/ particle –to-surfactant interaction – dispersion (surface modification) by additives to the particle system.

There will of course be a competition between these two types of interaction – the degree of dispersibility and subsequent stability of a nanoparticle dispersion will thus be dependent on the system dynamics as well as on the interaction energies and steric factors. In order to attain a well-dispersed & stable system the re-agglomeration of the particles needs to be minimized.

The dispersion of the nanoparticle systems may include

- 1/ generation of primary particles
 - the (mechanical) step of breaking down of agglomerates if particles are added from the dry state or
 - in-situ generation of the particles (sol-gel, addition of liquid precursor etc),
- 2/ stabilization of the nanoparticle system in the fluid to prevent any re-agglomeration. This process may include modification of the particle surface by chemisorption of appropriate molecules with/without functional groups.

5.1.1 Dispersion/modification of nanoparticles

The present compilation of possible dispersion/modification procedures is focused on the targeted use of the particles for coatings and paints – i.e. well-dispersed systems which have to maintain a certain level of low viscosity to be applicable in the fluid state. The compilation is based on reviewing of the attached literature.

In general, the preparation of dispersions is quite challenging, the powders often do not wet or deagglomerate easily in the dispersing fluid medium. Pretreatment to deflocculate the nanopowder may require dispersants that need to be selected based on the surface chemistry of the powders. As mentioned above, powder suspension often requires a homogenization procedure (e.g.,

ultrasonics) to further break up aggregates. However, this process could also break up physically welded agglomerates, skewing the true particle size distribution of the material.

5.1.2 Dispersion and surface modification methods

The techniques listed include those used for dispersion or modification of the nanoparticles supplied in dry state but also characterization methods for the liquid-state nanoparticle dispersed systems such as colloidal silica.

5.1.3 Dispersion of dry particle systems - mechanical

Many nanomaterials are produced in a dry process. As a result, the particles need to be mixed into liquid formulations. This is where most nanoparticles form agglomerates during the wetting.

1/ wet milling (mechanical media)

Conventional processing devices, e.g. high-shear or rotor-stator mixers, high-pressure homogenizers or colloid and disk mills fall short in separating the nanoparticles into discrete particles. For weak agglomerates – and when combined with other techniques below – the wet milling (with balls or so-called cylpebs) can be an appropriate baseline method.

2/ ultrasound dispersion

In particular for small particulates, from several nanometres to couple of microns, ultrasonic cavitation is very effective in breaking agglomerates, aggregates and even primaries – breaking the van der Waals forces in agglomerates and sometimes even primary particles.

The particle milling effect is based on intense ultrasonic cavitation. When sonicating liquids at high intensities, the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles, with rates depending on the frequency. During the low pressure cycle, high-intensity ultrasonic waves create small vacuum bubbles or voids in the liquid.

When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a high pressure cycle. This phenomenon is termed cavitation. The implosion of the cavitation bubbles results in microturbulences and micro-jets of up to 1000km/h. Large particles are subject to surface erosion (via cavitation collapse in the surrounding liquid) or particle size reduction (due to fission through interparticle collision or the collapse of cavitation bubbles formed on the surface). This leads to sharp acceleration of diffusion, mass-transfer processes and solid phase reactions due to crystallite size and structure changing.

Ultrasound can be applied for the effective dispersing of high concentration master-batches – processing low and high viscosity liquids. This makes ultrasound good processing solution for paints and coatings, based on different media, such as water, resin or oil.

5.1.4 Dispersion of dry particle systems - chemical

The dispersion procedure over the chemical route may always include a mechanical treatment according, either as a pre-treatment or in parallel to the addition of the dispersing agents.

1/ Dispersion by direct surface interaction with dispersants

Many different procedures available depending on the basic/acidic nature of the particle surface, different types of stabilization such as:

- Electrostatic (mainly aqueous systems)
- Steric
- Combined

In both aqueous and non-aqueous environments, the possible use of polymers for stabilizing particles in suspension largely depends on the nature of the side chains. In general, there are three mechanisms by which polymers can stabilize colloidal suspensions:

- steric stabilization
- electrosteric stabilization
- depletion stabilization

Using polymers, electrosteric stabilization is the most common mechanism for stabilizing particles in polar liquids, in apolar liquids steric stabilization is most common. However, the influence of depletion stabilizations mechanisms should not be overlooked. The influence of other parameters (pH, solids loading, temperature, etc.) on stabilization plays also an important role. An example of this is the influence of the molecular weight of the polymer. It has been proven that steric stabilization is high enough by itself to fully stabilize a colloidal suspension only if the molecular weight of the polymer macromolecules is higher than 10000. This provides a sufficiently thick steric barrier. Otherwise, coagulation due to the van der Waals forces would take place. In this case the polymer also has to be strongly anchored to the surface.

2/ Surface modification by coupling agents

is applied to improve the dispersion performance; a strong chemical bond is created between the particle surface and the coupling agent; the functional groups of the coupling agent interact with the additional dispersing agents. The compatibility between the fillers and the polymer matrix can be enhanced by grafting organic groups on the surface of the fillers. Grafting of the particles refers to the processes involving the interaction of the coupling agent and the dispersant and/or the coating matrix.

For this purpose, a special class of chemicals is available: silane coupling agents. Silane coupling agents have a silicon centred group that can form chemical or physical bonds with a metal oxide surface, and they have an organic group for a good compatibility with organic materials. The organic group may be a simple alkyl chain but it may also contain a functional group, such as an amine, an epoxy, or a methacrylate group. This organo-functional group can be used for further reaction with other organic materials.

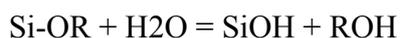
As an example, to improve the compatibility of the nanosized fillers with the acrylate matrix, the surface of the fillers can be treated with silane coupling agents. Polycarbonate can be used as a substrate - there is a strong commercial interest in this coating-substrate combination. Polycarbonate is an interesting material to replace glass in numerous applications as it is highly transparent, flexible, has a high impact resistance, and is easy to process. But it has also low scratch and abrasion resistance and accumulation of electrostatic charge – properties which can be corrected by nanoparticle-containing coatings.

Surface coverage: An important question is how much a silane e.g. such as typically used MethacryloxyPropyltrimethoxySilane (MPS) is required to cover the surface of the particles. Theoretical calculations yield different estimates, depending on the orientation of the MPS molecules. The real values can deviate from these estimates due to incomplete coverage or as a result of the formation of multilayers. In literature most studies describe the modification of silica while only a few consider the modification of other metal oxides. Only a part of these studies mention the quantitative amount of grafted molecules (experimentally determined maximum values for the surface coverage of oxides by MPS range from 2.8 $\mu\text{mol}/\text{m}^2$ to 7.5 $\mu\text{mol}/\text{m}^2$, depending on the type of metal oxide).

Grafting reactions: MPS and the other silane coupling agents can be represented by the general formula:



The C-Si bond is relatively stable and will not react under ambient conditions. The Si-OR bond, however, is easily hydrolyzed with the formation of a silanol group and an alcohol as a result:



The hydrolysis reaction is reversible, and the reverse reaction can also proceed with other alcohols. However, typically these reactions are performed with a large excess of water and in this case virtually all alkoxy groups on the silane are hydrolyzed. The hydrolysis reaction is catalyzed both by acid and base and the minimum hydrolysis rate is found at pH 7.

5.1.5 Dispersion in wet systems

Sol-gel-based processes and other liquid state reactions.

These techniques are quite frequent and convenient as they can circumvent the problem of agglomeration & dispersion of dry systems.

5.2 Conclusions from screening tests and further development

Incompatibility and difficulties to obtain homogeneous dispersions were encountered with some of the nanoparticles when modifying paints like UV curing clear coat solvent borne systems.

More generally,

- Homogeneous dispersions were more difficult to obtain when nanosized powders were applied compared with sols. Adequate dispersion methods must be developed for each case
- Coatings for consumer electronics applications:
 - High demanding specifications and hard reference coatings
 - No higher technical performance observed so far even when enough compatibility was reached
 - Improving scratch resistance without deteriorating another property (e.g. visual aspect) is demanding and not achieved yet
- Coatings for concrete flooring:
 - Little improvement is observed with some nanoparticle systems
 - Covalent bonds between modifier particle and matrix are needed in order to provide mechanical strength improvement
- Coatings from interior trim/wall/floor applications:
 - Significant improvements have been observed when some test methods are used
 - Modification of the coating at an early stage of the formulation is advantageous

6 Testing of scratch resistance

Different methods available in the project were used to detect:

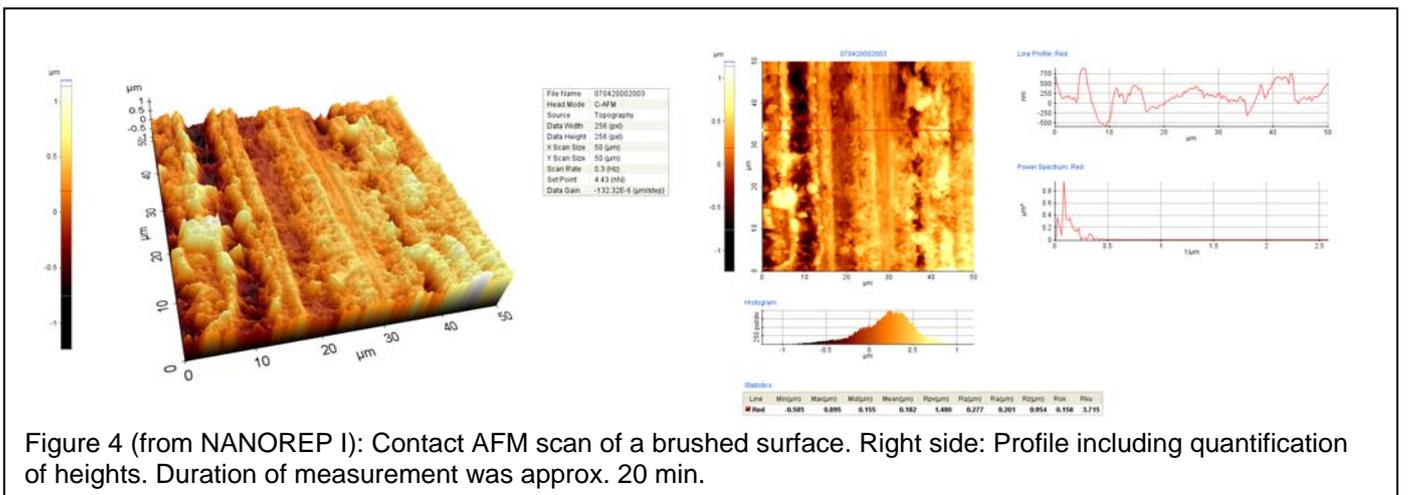
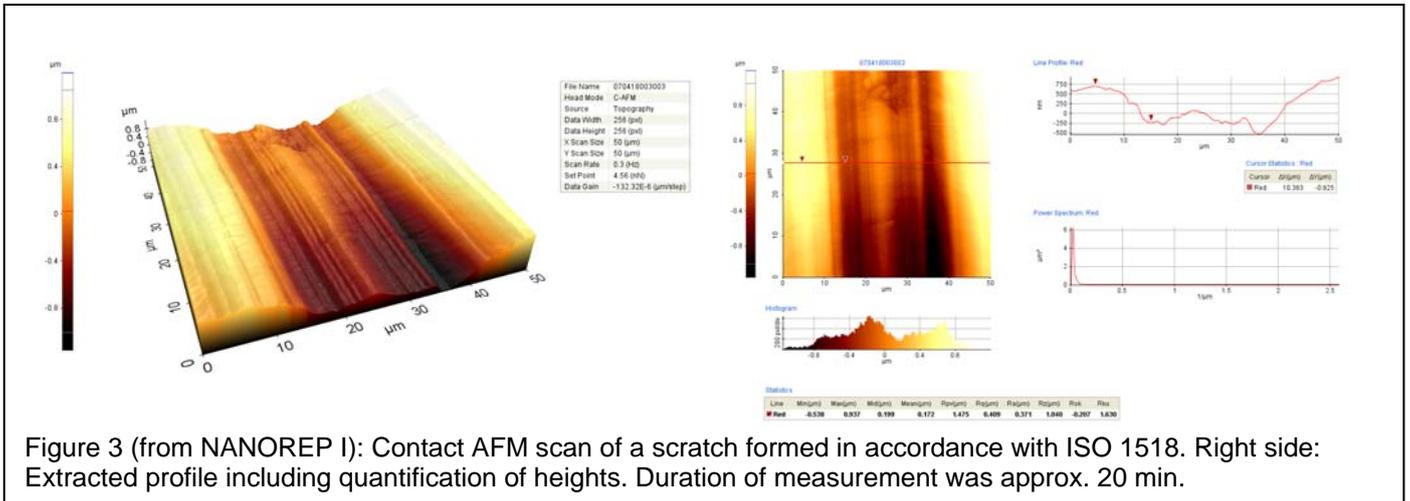
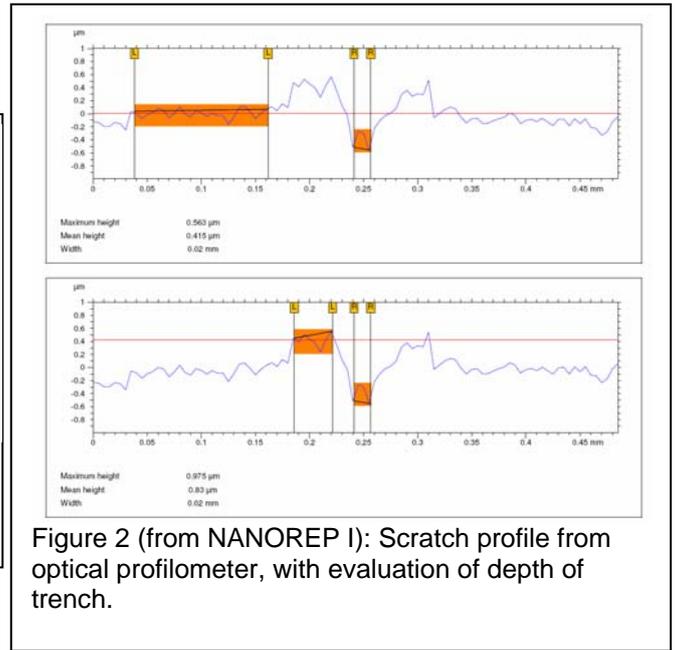
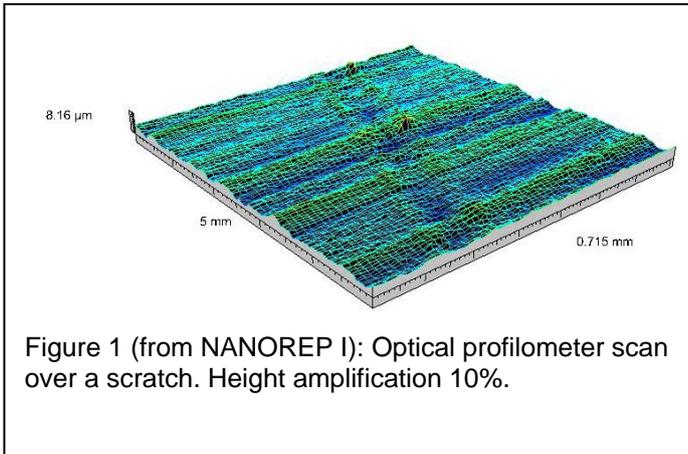
- Visible scratch, with naked eye or magnification
- Change in gloss
- Weight loss
- Topography (type of surface damage)
- Poor reproducibility

The methods of determination of topology (AFM), composition (ESCA) and microscratch resistance (scratch AFM) of surface formed of nanoparticles modified polymers have been applied for the characterization of materials prepared in the project.

Characterization of surface finish and scratches were performed with naked eye, magnification, using optical profilometry and atomic force microscopy, as illustrated in Fig. 3-6.

Samples were scratched in accordance to ISO 1518 and the surface evaluated with naked eye and suitable magnification. To investigate arrays of scratches as well as single scratches over distances of several millimetres, and getting a first impression of scratch type and structure, a non-contact optical profiling system was used. The system used the wavelength of light reflected by the surface to measure height differences. Clear, colourless coatings were gold sputter-coated.

An atomic force microscope was used to investigate scratch characteristics more thoroughly, including topographical features indicating scratch or deformation type. Quantification of depths and widths of scratches down to a nanometre level was performed. Contact as well as non-contact modes were utilized.



Conclusion: We have improved our understanding of scratches and influence of hard particles on scratch resistance and other properties of paint. A comprehensive understanding of the nature of scratching is essential for success.

7 Health, Safety and Environment

7.1 NP statement at EKA

[..\EKA\NP Statement 2007-06-04_2_.pdf](#)

7.2 Summary report

IVF was responsible for summarizing the issues related to the impact of handling and using of the nanoparticles in the area of health, safety and environment (HSE). The investigation of this issue which was performed includes a collection of selected articles found by literature search (posted in the eRoom) and the summary report below.

7.2.1 Background

The nanoparticle area has experienced a tremendous growth not only in the R&D field but also in large scale applications thus becoming part of the product flow from the production development to the waste management. Manmade nanoparticles range from the well-established multi-ton production of carbon black and fumed silica for applications in plastic fillers and car tires to microgram quantities of fluorescent quantum dots used as markers in biological imaging. Many types of nanoparticles have been used for tenths of years without either noticing or monitoring their health, safety or, in a broader sense, environmental effects – not at least because the nano-aspect has not been put in the foreground the way it has been done during the last 10 years. One such example is silica and other sols or dispersions – these particles in the nano-range have been in large scale use since 20 –30 years without any records of negative impact. However, in addition to these and few others there is a large number of completely new –either natural or synthetic particles in the nano-range which have – in addition to their positive technical effects – also attracted attention in relation to their potential hazardous impact. The report below summarizes some current HSE activities directed to catch up with the rapid technical and commercial development - the discussion of the potential effects of the widespread use of nanoparticles in the consumer and industrial products are just beginning to emerge. Most of these activities are going on within the industrialized countries of EU community and the USA.

7.2.2 Risk areas

The number of detailed studies is limited but there are some attempts to summarize the status e.g. “Nanoparticles – known and unknown health risks” by Hoet et al (Journal of Nanobiology, Dec. 2004).

The following is concluded:

“Particles in the nano-size range can certainly enter the human body via the lungs and the intestines; penetration via the skin is less evident. It is possible that some particles can penetrate deep into the skin. The chances of penetration depend on the size and surface properties of the particles and also on the point of contact in the lung, intestines or skin. After the penetration, the distribution of the particles in the body is a strong function of the surface characteristics of the particles. A critical size might exist beyond which the movement of the nanoparticles in parts of the body is restricted.”

There is also an excellent and very detailed recent report (in Swedish) from the Swedish Chemical Inspection Agency: **Nanoteknik: – stora risker med små partiklar?** - En kunskapssammanställning om risker med nanoteknik för hälsa och miljö, samt förslag till hur identifierade kunskapsluckor bör åtgärdas (Rapport Nr 6/07, www.kemi.se). This report outlines in very much detail the current state-of-the-art.

There are some few reports outlining specific risks, in an article entitled “Nanoparticles could have a negative effect on plant growth” (Nanowerk Spotlight, March 2007), it is pointed out that in order to develop a comprehensive toxicity profile for manufactured nanoparticles, their phytotoxicity – the ability to cause injury to plants – has to be investigated. A new study examined the effects of five types of nanoparticles on seed germination and root growth of six higher plant species and observed that several types of the particles had significant inhibition on seed germination and root growth of the six plants.

7.2.3 Government actions

Governments are also using services of private consultancy firms to define the roadmap for future measures. One such large effort activity is with the international firm ICF International (www.icfi.com) contracted to address this issue under the title: “Environmental, Health, and Safety Implications of Nanotechnology: Where Should the Federal Government Go From Here?”.

Their specific report, although considering the US-specific environment, is particularly valuable as it addresses the general issues of implementation – in particular, it points out that any significant progress requires prompt initiation and management of building a plan for a large and well-integrated HSE research program. In addition, they point at two types of approaches that both can have an adverse effect on the nanotechnology policy

1/ Policymakers could assume nanotechnology is essentially safe and allow widespread commercialization, only to later discover significant health or environmental effects, akin to those of asbestos, lead, and CFCs,

2/ Policymakers could assume nanotechnology is very risky and prohibit most uses, foregoing the benefits of the new technology and undermining national competitiveness, only to later find that the concerns were unfounded.

Both types of policy mistake could have significant social and economic consequences. What’s more, a well-designed and implemented EHS research strategy can go a long way toward minimizing the chance of either type of policy mistake.

In the US, based on federal government's September 2006 report, Environmental, Health, and Safety:

Research Needs for Engineered Nanoscale Materials, new priorities are drawn have an adequate risk research strategy to ensure that nanotechnology is being commercialized safely. The Environmental Protection Agency (EPA) recently stated that nanotechnology must be subject to an adequate oversight system—a system designed to identify and minimize any adverse effects of nano materials and products on health or the environment.

7.2.4 General measures

Within the EU community a consultation on a voluntary code of conduct has been launched that researchers and companies can use when developing nanotechnology products. In formulating the code the European Commission is calling on scientists, industry, policy-makers, media and the general public to contribute to the growing debate about the benefits and potential harmful effects of the technology. The HSE issues are also addressed in the “Nanosciences and Nanotechnologies: An action plan for Europe 2005-2009”.

NIOSH’s Nanotechnology Research Center (NTRC, USA) is involved in efforts concerning the occupational safety and health perspectives of engineered nanomaterials. Their activities are based on the fact that collaboration is the key to protecting nanotechnology workers. Several simple

guidelines have been issued by companies interacting with NTRC, a good example is the company Altair-nano's plan:

- Ensure employees exposed to nanomaterials are completely covered with PPE (Personal Protective Equipment).
- Install an automated transfer system where manual processes exist.
- Use HEPA (High Efficiency Particulate Air) filtration in vacuums and ensure all gaskets are properly sealed.
- Employ respiratory protection when using and servicing vacuums.
- Make ventilation systems and hoods more effective.
- Have a dedicated area for cleaning off overcoats.
- Ensure that people with long hair wear covers to prevent accumulation of particulates in the hair and scalp.
- Install and use sticky mats to reduce dust in areas.
- Maintain negative pressure differentials in all areas.

As another action in the HSE field a Nanoethics Group(www.nanoethics.org) has been formed - a research organization to study nanotechnology's impact on society and related ethical issues. Including professional ethicists, they help to identify and evaluate possible harms and conflict as well as to educate and advise both organizations and the broader public on these issues as a foundation to guide policy and responsible research.



norden

Nordic Innovation Centre

Nordic Innovation Centre

The Nordic Innovation Centre initiates and finances activities that enhance innovation collaboration and develop and maintain a smoothly functioning market in the Nordic region.

The Centre works primarily with small and medium-sized companies (SMEs) in the Nordic countries. Other important partners are those most closely involved with innovation and market surveillance, such as industrial organisations and interest groups, research institutions and public authorities.

The Nordic Innovation Centre is an institution under the Nordic Council of Ministers. Its secretariat is in Oslo.

For more information: www.nordicinnovation.net